Two Different (Oxalato)(bipyridine)copper(II) Complexes in One Single Crystal. Crystal Structures and Magnetic Properties of $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]X_2\cdot[Cu(bipy)(C_2O_4)]$ ($X = NO_3^-$, BF_4^- or ClO_4^-)†

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Three complexes of formula $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]X_2\cdot[Cu(bipy)(C_2O_4)]$ (bipy = 2,2'-bipyridine; $C_2O_4^{2-}$ = oxalate, $X = NO_3^-$ **1**, BF_4^- **2** or ClO_4^- **3** have been synthesised and their crystal structures determined by single-crystal X-ray diffraction methods at room temperature. They are all isostructural and crystallize in the monoclinic system, space group $C2/c$, $Z = 4$, with $a = 21.739(2)$, $b = 10.458(1)$, $c = 16.023(2)$ Å, $\beta = 95.69(1)°$ for **1**, $a = 22.740(5)$, $b = 10.508(1)$, $c = 16.129(2)$ Å, $\beta = 92.32(1)°$ for **2**, and $a = 22.819(3)$, $b = 10.583(2)$, $c = 16.389(2)$ Å, $\beta = 91.52(2)°$ for **3**. The crystal structures of **1** and **2** were determined from Patterson and Fourier analysis and refined by full-matrix least-squares techniques, whereas that of **3** was solved by direct methods. Final values of the reliability factors R (R') were 0.029 (0.051) for **1**, 0.033 (0.046) for **2** and 0.057 (0.059) for **3** with 3290, 3526 and 1972 observed reflections respectively. Their structures consist of cationic centrosymmetric dinuclear $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]^{2+}$ units, neutral axiosymmetric mononuclear $[Cu(bipy)(C_2O_4)]$ entities and either NO_3^-, BF_4^- or ClO_4^- as counter ion. Each copper atom of the dinuclear species is in a square-pyramidal environment with two oxalate oxygen and two bipyridine nitrogen atoms as a base and a water molecule at the apical position. The copper atom of the mononuclear complex is in a slightly tetrahedrally distorted square comprised of two bipyridine nitrogen and two oxalate oxygen atoms. In both complexes one or two more distant atoms of the counter ion completes a (5 + 1) or a (4 + 2) copper co-ordination, respectively. The mono- and di-nuclear entities form an alternating chain *via* weak interactions through counter ions and copper atoms. Variable-temperature (20–300 K) magnetic susceptibility measurements revealed a strong antiferromagnetic interaction within the dinuclear unit, the singlet–triplet energy gap being −386, −378 and −376 cm⁻¹ for **1**, **2** and **3**, respectively. The $\chi_M T$ *versus* T curve for all three complexes exhibits a plateau at $T < 80$ K which corresponds to the Curie law expected for the mononuclear complex. The magnitude of the exchange coupling in this series has been analysed in the framework of a simple orbital model.

Some years ago, at the beginning of our studies of the exchange interaction propagated by extended bridges, we described the synthesis, crystal structures and magnetic properties of a series of oxalato-bridged copper(II) dinuclear complexes.[1] A strong antiferromagnetic coupling was achieved between paramagnetic centres in spite of the large (> 5 Å) intramolecular copper–copper separation. This work showed that it is possible to tune the singlet–triplet energy gap in μ-oxalato dinuclear copper(II) complexes over a wide range: values between zero and −385.6 cm⁻¹ were attained by keeping the $Cu(\mu\text{-}C_2O_4)Cu^{2+}$ unit and playing on the nature of the terminal ligands. The plasticity of the co-ordination sphere of copper(II) allows such a metal ion to adopt various stereochemistries and consequently different orientations of the resulting magnetic orbitals with respect to the symmetry-adapted molecular orbitals of the bridge. So the overlap between the two magnetic orbitals in the dinuclear unit can be modified and the magnitude of the antiferromagnetic interaction, which is expected to vary as the square of this overlap,[2–4] tuned by using the terminal ligands as adjusting screws. A second example of tunable exchange dealing with μ-oxamido dinuclear copper(II) complexes[5] was also reported for which single-triplet energy gaps up to −440 cm⁻¹ were reached. Other factors such as the number and nature of the unpaired electrons of the interacting metal ions[6–8] as well as the nature of the atoms of the oxalato-type bridge[9–11] were analysed. More recently, we have observed that the last factor to be considered, that is the nature of the counter ion, is an unexpected but very efficient tool to tune the exchange interaction in copper(II)–oxalate–2,2'-bipyridine complexes[12] and theoretical calculations have proved useful to predict and correlate structural modifications and magnetic properties in oxalato-bridged copper(II) complexes.[13]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

In our attempts to synthesise this series of complexes we obtained single crystals of $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]X_2 \cdot [Cu(bipy)(C_2O_4)]$ (bipy = 2,2′-bipyridine; $C_2O_4^{2-}$ = oxalate; X = NO_3^- **1**, BF_4^- **2** or ClO_4^- **3** where both mono- and di-nuclear complexes are present in the same unit cell. We report here on the synthesis, crystal structures and magnetic properties of these complexes. A preliminary communication concerning the nitrate complex[14] and a solution study[15] on the formation of $[Cu(bipy)(C_2O_4)]$ and $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]^{2+}$ have been published.

Experimental

Materials.—Copper(II) nitrate trihydrate, perchlorate hexahydrate, 2,2′-bipyridine, oxalic acid dihydrate and lithium hydroxide monohydrate were of reagent grade and used without further purification. Copper(II) tetrafluoroborate was obtained by exchange through a Lewatitt S100 cation-exchange resin. The procedure used was as follows: as the resin was initially in the hydrogen form, an aqueous solution of 0.4 mol dm^{-3} copper(II) sulfate was passed through the column containing the cationic exchange resin (5 g) in order to exchange H^+ by Cu^{2+}. When the pH of the effluent was the same as that of the initial copper(II) solution, the column was thoroughly washed until no sulfate was detected in the waste. Finally, a concentrated aqueous solution of ammonium tetrafluoroborate (4 mmol, 10 cm^3) was allowed slowly to drip into the column and water was used to elute the tetrafluoroborate solution. Thus a blue aqueous solution containing 2 mmol of copper(II) tetrafluoroborate (*ca.* 70 cm^3) was obtained.

Analytical data (C,H,N) were obtained by the Servei de Microanàlisi Elemental (CSIC, Barcelona, Spain). The copper content was determined by atomic absorption spectroscopy.

Synthesis of the Complexes.—$[Cu_2(bipy)_2(H_2O)_2(C_2O_4)][NO_3]_2 \cdot [Cu(bipy)(C_2O_4)]$ **1**. A warm aqueous solution of $Li_2C_2O_4$ (1 mmol, 25 cm^3) was added to aqueous $Cu(NO_3)_2 \cdot 3H_2O$–2,2′-bipyridine (1:1, 2 mmol, 100 cm^3) with continuous stirring. The hot solution was filtered and the dark blue filtrate allowed to evaporate at room temperature. A mixture of rhombohedral dark blue crystals of complex **1** and blue rods of the chain complex $[Cu(bipy)(C_2O_4)] \cdot 2H_2O$[16] was deposited after a few hours. They were separated by hand, washed with cold water and dried over calcium chloride. The Cu^{2+}:bipy:$C_2O_4^{2-}$ molar ratio was varied over a wide range in order to improve the yield and quality of the crystals and 1:1:0.5 appeared to be the best. The presence of greater amounts of oxalate in the synthetic process led to the ready precipitation of the insoluble compound $[Cu(bipy)(C_2O_4)] \cdot 2H_2O$ and lower contents to a very low yield of **1** (Found: C, 40.90; H, 2.90; Cu, 19.25; N, 11.15. Calc. for $C_{34}H_{28}Cu_3N_8O_{16}$: C, 41.05; H, 2.80; Cu, 19.15; N, 11.25%).

$[Cu_2(bipy)_2(H_2O)_2(C_2O_4)][BF_4]_2 \cdot [Cu(bipy)(C_2O_4)]$ **2**. The preparation of complex **2** was similar to that for **1** with the exception that copper(II) was added in the form of copper(II) tetrafluoroborate solution. The complex crystallizes as dark blue polyhedra together with the crystals of $[Cu(bipy)(C_2O_4)] \cdot 2H_2O$ (Found: C, 39.05; H, 2.65; Cu, 18.05; N, 7.95. Calc. for $C_{34}H_{28}B_2Cu_3F_8N_6O_{10}$: C, 39.10; H, 2.70; Cu, 18.25; N, 8.05%).

$[Cu_2(bipy)_2(H_2O)_2(C_2O_4)][ClO_4]_2 \cdot [Cu(bipy)(C_2O_4)]$ **3**. An aqueous solution of $Li_2C_2O_4$ (0.39 mmol, 10 cm^3) was added to a methanolic suspension of $[Cu(bipy)][ClO_4]_2$ (0.64 mmol, 40 cm^3) with continuous stirring. The solid dissolved progressively and the initial pale blue colour turned dark blue upon addition of oxalate. At the end of the addition a slight precipitate was formed which dissolved by dilution with water (final volume of the methanol–water mixture 80 cm^3). A mixture of dark blue parallelepipeds of complex **3** and blue rods of $[Cu(bipy)(C_2O_4)] \cdot 2H_2O$ was deposited by slow evaporation of the resulting solution at room temperature. They were separated by hand, washed with cold water and dried over calcium chloride (Found: C, 38.05; H, 2.60; Cu, 17.70; N, 7.70. Calc. for $C_{34}H_{28}Cl_2Cu_3N_6O_{18}$: C, 38.15; H, 2.60; Cu, 17.80; N, 7.85%).

Physical Techniques.—Infrared spectra were taken on a Perkin Elmer 1750 FTIR spectrometer as KBr pellets. Magnetic susceptibility measurements were carried out in the 20–300 K temperature range by means of a Faraday-type magnetometer equipped with a helium-flow cryostat. The independence of the susceptibility on the magnetic field was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. Corrections for the diamagnetism of the complexes were estimated from Pascal's constants[17] to be -441×10^{-6}, -444×10^{-6}, and -477×10^{-6} cm^3 mol^{-1} for complexes **1**, **2** and **3**, respectively. X-Band EPR spectra were recorded, both at room temperature and at 4 K, with a Brüker ER200 spectrometer equipped with a helium continuous-flow cryostat. The magnetic field was determined with a Hall probe and the kylstron frequency with a Hewlett-Packard frequency meter.

Crystal Data and Structure Refinements.—Single crystals were mounted on a Enraf–Nonius CAD4 computer-controlled four-circle diffractometer in Toulouse (complexes **1** and **2**) and on a Philips PW-1100 diffractomer in Barcelona (**3**), using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). Crystal data including the space group deduced from systematic absences and accurate unit-cell constants derived from least-squares refinements of the setting angles of 25 reflections are listed in Table 1, along with other relevant crystallographic features. The intensities of three standard reflections measured every 2 h showed no significant variations. Scan modes of θ–1.33θ and θ–2θ for **1** and **2**, respectively, and an ω-scan technique for **3** were used to collect intensity data, the maxima θ values being 29 (**1**), 30 (**2**) and 25° (**3**). Lorentz polarization but no absorption corrections were made. Of the 4006 (**1**), 4403 (**2**) and 1983 (**3**) measured independent reflections, 3290 (**1**), 3526 (**2**) and 1972 (**3**) were unique with $I > 3\sigma(I)$ for **1** and **2** and $I > 2.5\sigma(I)$ for **3** and were used for the structure refinements.

Structure refinements of complexes **1** and **2** were carried out by full-matrix least-squares techniques, starting with the positions of the heavy atoms determined from the experimental Patterson function, and using Fourier and Fourier difference synthesis to locate the lighter atoms. The structure of **3** was solved by direct methods using the MULTAN 84 system.[18] The calculations were performed using SDP (**2**), SHELX 76 (**1** and **3**) and ORTEP programs.[19–21] The atomic scattering factors were taken from the usual tabulation,[22] and the effects of the anomalous scattering were taken into account by using Cromer and Ibers' values of $\Delta f'$ and $\Delta f''$.[23] Throughout the refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure-factor amplitudes. A secondary extinction coefficient was introduced in the final stage of the refinement. The weights (w) as well as the final values of the reliability factors (R and R') for complexes **1**–**3** are listed in Table 1.

The non-hydrogen atoms were treated as anisotropic scatterers. Hydrogen atoms were introduced as fixed contributors at idealised positions for the 2,2′-bipyridine groups (C–H 0.95 Å) or at positions located on Fourier difference maps for the water molecules in complexes **1** and **2**, and they were given isotropic thermal parameters equal to the equivalent B values of atoms to which they are attached. Hydrogen atoms were not found in complex **3**. In **1** one nitrate oxygen atom was found distributed over two positions whose occupancies were refined. Refined positional parameters for non-hydrogen atoms are given in Tables 2, 3 and 4 for complexes **1**, **2** and **3**, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 1 Summary of crystal data, intensity-data collection and structure refinement for complexes **1**–**3**

Compound	**1**	**2**	**3**
Formula	$C_{34}H_{28}Cu_3N_8O_{16}$	$C_{34}H_{28}B_2Cu_3F_8N_6O_{10}$	$C_{34}H_{28}Cl_2Cu_3N_6O_{18}$
M	995.27	1044.87	1070.16
a/Å	21.739(2)	22.740(5)	22.819(3)
b/Å	10.458(1)	10.508(1)	10.583(2)
c/Å	16.023(2)	16.129(2)	16.389(2)
β/°	95.69(1)	92.32(1)	91.52(2)
U/Å^3	3625	3851	3956
D_c/g cm^{-3}	1.824	1.802	1.796
μ(Mo-Kα)/cm^{-1}	18.36	17.48	18.85
F(000)	1006	1046	1078
Crystal size (mm)	0.40 × 0.28 × 0.21	0.35 × 0.27 × 0.18	0.42 × 0.15 × 0.20
Take-off angle/°	2.7	2.8	2.0
Standard reflections used every 3600 s	2 0 4, 3 1 4, 6 0 0	10 0 0, 0 0 6, 4 6 2	4 2 0, 1 1 1, −2 4 6
Standard reflections used every 100 reflections	9 9 0, 22 −1 3, 16 0 0	20 0 0, 0 10 0, 0 0 14	4 2 0, −1 1 1, −2 4 6
No. of variables	295	286	289
Weighting scheme	$[\sigma^2(F_o) + 0.002\,07F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.0012F_o^2 + 3]^{-1}$	$[\sigma^2(F_o) + 0.0003F_o^2]^{-1}$
E.s.d. in an observation of unit weight (electron)	1.09	0.95	1.23
$R(= [\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert])$	0.029	0.033	0.057
$R'\{= [\Sigma w(\Delta F)^2/\Sigma\lvert F_o\rvert^2]^{\frac{1}{2}}\}$	0.051	0.046	0.059

* Details in common: monoclinic, space group $C2/c$; $Z = 4$; $T = 25$ °C.

Table 2 Positional parameters and their estimated standard deviations (e.s.d.s) for complex **1**

Atom	x	y	z
Cu(d)	0.201 83(1)	0.105 44(2)	0.106 39(1)
O(wd)	0.105 25(8)	0.138 9(2)	0.046 8(1)
O(1d)	0.227 05(7)	0.286 8(1)	0.097 66(9)
O(2d)	0.234 82(7)	0.086 6(1)	−0.003 42(9)
C(d)	0.247 54(9)	0.308 0(2)	0.029 7(1)
N(2d)	0.177 33(8)	0.115 7(2)	0.222 0(1)
N(2′d)	0.194 12(8)	−0.080 9(2)	0.127 5(1)
C(1d)	0.165 27(9)	0.001 2(2)	0.256 0(1)
C(3d)	0.166 3(1)	0.222 8(2)	0.263 7(1)
C(4d)	0.142 1(1)	0.220 7(2)	0.340 5(2)
C(5d)	0.129 4(1)	0.103 8(2)	0.374 9(2)
C(6d)	0.141 4(1)	−0.007 8(2)	0.332 4(1)
C(1′d)	0.176 84(9)	−0.110 1(2)	0.202 8(1)
C(3′d)	0.202 5(1)	−0.175 7(2)	0.073 0(1)
C(4′d)	0.193 6(1)	−0.302 8(2)	0.092 6(2)
C(5′d)	0.177 1(1)	−0.331 9(2)	0.170 8(2)
C(6′d)	0.168 8(1)	−0.236 1(2)	0.227 1(1)
Cu(m)	0	0.485 76(3)	1/4
O(1m)	0.021 83(9)	0.352 4(1)	0.176 8(1)
O(2m)	0.025 05(9)	0.141 5(2)	0.172 3(1)
C(m)	0.013 52(9)	0.241 0(2)	0.206 9(1)
N(2m)	0.015 13(8)	0.625 2(2)	0.173 3(1)
C(1m)	0.007 95(9)	0.743 0(2)	0.206 8(1)
C(3m)	0.028 4(1)	0.613 9(2)	0.094 0(2)
C(4m)	0.034 7(1)	0.718 9(2)	0.043 9(2)
C(5m)	0.028 2(1)	0.838 1(2))	0.077 4(2)
C(6m)	0.014 4(1)	0.851 7(2)	0.159 2(2)
N(n)	0.125 6(1)	0.573 2(2)	0.406 0(1)
O(1n)	0.128 75(9)	0.690 8(2)	0.417 1(1)
O(2n)	0.112 0(1)	0.499 6(2)	0.459 5(1)
O(3n)[a]	0.120 3(2)	0.528 4(3)	0.330 2(2)
O(4n)[b]	0.166 2(3)	0.534 3(5)	0.352 6(3)

[a] Occupancy 0.61. [b] Occupancy 0.39.

Results and Discussion

Description of the Structures.—The three compounds are isostructural. They are made of three components in ratios 1:1:2, (*i*) cationic dinuclear $[(bipy)(H_2O)Cu(O_2C_2O_2)Cu(H_2O)(bipy)]^{2+}$ centrosymmetric units (Fig. 1), (*ii*) neutral mononuclear $[(bipy)Cu(O_2C_2O_2)]$ axiosymmetric units (Fig. 2), and (*iii*) either NO_3^-, BF_4^- or ClO_4^- as a counter ion. Main features of both the mono- and di-nuclear entities in the nitrate derivative were sketched in a previous short paper.[14]

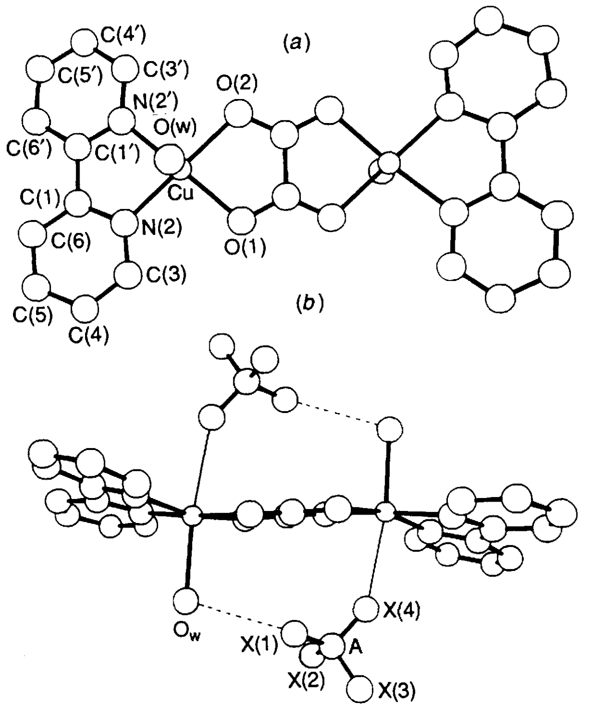

Fig. 1 Top (*a*) and side (*b*) view of the centrosymmetric dinuclear cationic complex $[Cu_2(bipy)_2(H_2O)_2(C_2O_4)]^{2+}$ (atoms labelled d in text and tables)

Bond lengths, angles and atom-to-plane distances are synoptically displayed in Tables 5, 6 and 7, respectively.

In the dinuclear species (atoms labelled d) the Cu(d) atoms are in a square-pyramidal environment with two oxalate oxygen and two 2,2′-bipyridine nitrogen atoms as a base and a water molecule at the apex. Elevations of the Cu(d) atoms above the mean basal planes are given in Table 7 which also shows atom-to-plane distances for the pyramid bases and oxalate bridges with the corresponding dihedral angles. In the mononuclear species (atoms labelled m) the Cu(m) atom is in a slightly tetrahedrally distorted square environment formed by two 2,2′-bipyridine nitrogen and two oxalate oxygen atoms. Atom-to-plane distances are also given in Table 7. In both species one or two more distant atoms of the counter ion complete the copper

Table 3 Positional parameters and their e.s.d.s for complex **2**

Atom	*x*	*y*	*z*
Cu(d)	0.195 50(1)	0.103 40(3)	0.098 93(2)
O(wd)	0.103 34(9)	0.146 1(2)	0.045 4(1)
O(1d)	0.224 50(9)	0.281 2(2)	0.098 0(1)
O(2d)	0.225 47(8)	0.094 4(2)	−0.013 9(1)
C(d)	0.249 7(1)	0.304 0(2)	0.032 0(2)
N(2d)	0.172 0(1)	0.107 4(2)	0.215 6(1)
N(2′d)	0.185 87(9)	−0.082 8(2)	0.114 9(1)
C(1d)	0.160 6(1)	−0.008 1(3)	0.247 6(2)
C(3d)	0.161 4(1)	0.211 3(3)	0.260 0(2)
C(4d)	0.138 2(2)	0.204 2(3)	0.337 6(2)
C(5d)	0.126 0(2)	0.087 2(3)	0.370 1(2)
C(6d)	0.137 5(1)	−0.021 1(3)	0.325 2(2)
C(1′d)	0.172 3(1)	−0.116 2(3)	0.192 5(2)
C(3′d)	0.195 3(1)	−0.174 4(3)	0.059 6(2)
C(4′d)	0.191 3(1)	−0.301 9(3)	0.079 5(2)
C(5′d)	0.178 4(2)	−0.335 8(3)	0.158 3(2)
C(6′d)	0.169 1(2)	−0.241 7(3)	0.216 3(2)
Cu(m)	0	0.489 37(4)	1/4
O(1m)	0.022 21(9)	0.355 3(2)	0.176 9(1)
O(2m)	0.025 3(1)	0.145 2(2)	0.172 5(2)
C(m)	0.013 8(1)	0.246 1(2)	0.206 6(2)
N(2m)	0.016 08(9)	0.629 7(2)	0.173 4(1)
C(1m)	0.008 1(1)	0.745 7(2)	0.206 3(2)
C(3m)	0.029 5(1)	0.618 5(3)	0.094 3(2)
C(4m)	0.034 9(1)	0.723 9(3)	0.043 4(2)
C(5m)	0.027 3(1)	0.842 4(3)	0.076 8(2)
C(6m)	0.014 1(1)	0.854 8(3)	0.158 5(2)
B	0.133 5(2)	0.552 2(3)	0.389 6(2)
F(1)	0.127 0(1)	0.678 7(2)	0.408 2(1)
F(2)	0.111 3(2)	0.478 9(2)	0.448 6(2)
F(3)	0.104 34(9)	0.525 3(2)	0.314 4(1)
F(4)	0.191 1(1)	0.575 8(3)	0.377 7(2)

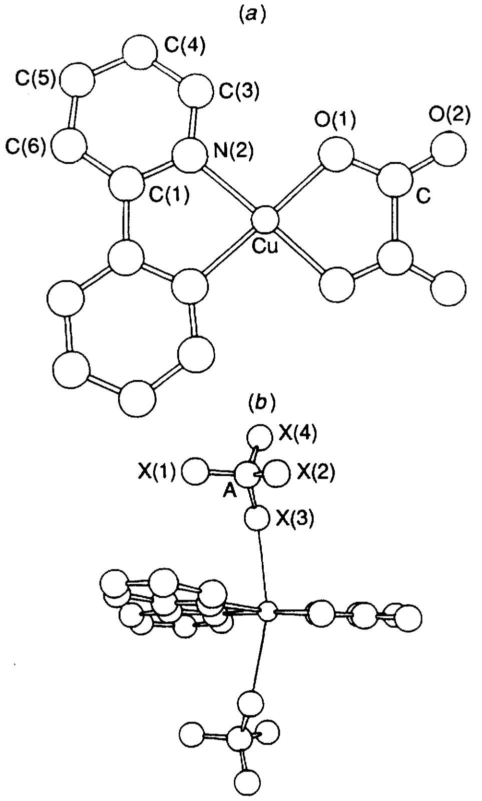

Fig. 2 Top (*a*) and side (*b*) view of the axiosymmetric mononuclear complex [Cu(bipy)(C_2O_4)]. The two-fold axis is horizontal (atoms labelled m in text and tables)

co-ordination to (5 + 1) and (4 + 2) respectively. This point will be dealt with later.

Table 4 Atomic positional parameters and their e.s.d.s for complex **3**

Atom	*x*	*y*	*z*
Cu(d)	0.693 54(3)	0.104 08(5)	0.596 03(3)
O(wd)	0.101 6(1)	0.348 9(2)	0.046 0(1)
O(1d)	0.723 8(1)	0.279 3(2)	0.597 2(1)
O(2d)	0.723 4(1)	0.096 3(2)	0.483 7(1)
C(d)	0.749 4(1)	0.197 9(3)	0.467 0(2)
N(2d)	0.670 9(1)	0.105 6(3)	0.712 6(2)
N(2′d)	0.684 1(1)	−0.081 5(3)	0.608 6(2)
C(1d)	0.660 1(1)	−0.011 3(3)	0.742 9(2)
C(3d)	0.660 2(2)	0.208 1(4)	0.757 8(3)
C(4d)	0.636 2(2)	0.199 5(4)	0.835 9(3)
C(5d)	0.624 8(2)	0.077 7(4)	0.867 3(2)
C(6d)	0.636 9(2)	−0.028 5(4)	0.821 0(2)
C(1′d)	0.671 9(1)	−0.118 1(3)	0.686 2(2)
C(3′d)	0.693 8(2)	−0.171 1(4)	0.550 9(3)
C(4′d)	0.690 0(2)	−0.299 1(4)	0.569 4(3)
C(5′d)	0.678 8(2)	−0.336 2(4)	0.649 8(3)
C(6′d)	0.669 8(2)	−0.244 6(4)	0.710 5(3)
Cu(m)	0	0.006 42(8)	1/4
O(1m)	−0.021 7(1)	0.139 7(2)	0.322 8(1)
O(2m)	−0.024 9(1)	0.349 1(2)	0.327 4(2)
C(m)	−0.012 9(1)	0.250 3(4)	0.294 3(3)
N(2m)	−0.015 8(1)	−0.134 7(3)	0.326 0(2)
C(1m)	−0.007 7(1)	−0.251 6(3)	0.294 2(2)
C(3m)	−0.028 3(2)	−0.122 0(4)	0.407 1(2)
C(4m)	−0.034 1(2)	−0.228 9(4)	0.457 1(3)
C(5m)	−0.027 1(2)	−0.348 4(3)	0.423 2(3)
C(6m)	−0.012 4(2)	−0.365 1(3)	0.340 9(3)
Cl	0.133 4(1)	−0.048 3(1)	0.387 0(1)
O(1)	0.128 6(1)	−0.179 4(3)	0.404 8(2)
O(2)	0.104 8(1)	0.023 4(3)	0.445 6(2)
O(3)	0.106 5(1)	−0.022 9(3)	0.308 1(2)
O(4)	0.192 1(1)	−0.012 4(3)	0.382 9(2)

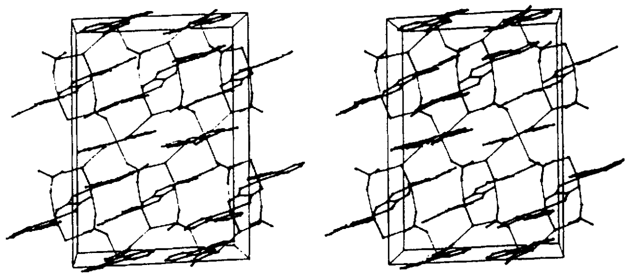

Fig. 3 Stereoscopic view down the *b* axis (*a* axis is vertical) of the molecular packing in [$Cu_2(bipy)_2(H_2O)_2(C_2O_4)$][$BF_4$]$_2$·[Cu(bipy)($C_2O_4$)] showing the intermolecular hydrogen-bonding network

The co-ordinated water molecules of the dinuclear entities are *trans* to each other according to the centrosymmetry. Each of them is doubly hydrogen-bonded (Tables 5 and 6) to the atom X(1) of a counter ion on the one hand and to one free oxygen atom O(2m) of the mononuclear species on the other. This latter interaction is duplicated through the two-fold axis so as to concentrate the two entities into an unlimited alternate chaining (Fig. 3).

In the tetrafluoroborate and perchlorate derivatives, both species are also alternately chained through weak interactions between AX_4^- counter ions and copper atoms (Fig. 3). The X(3) and X(4) atoms of each counter-ion complete the six-co-ordination of the copper atom of a mononuclear entity [Fig. 2(*b*)] and of one copper atom of a dinuclear entity [Fig. 1(*b*)] respectively. The corresponding Cu ··· X separations are larger than or equal to 2.6 Å (Table 5).

A question arises about the nitrato derivative: why does this compound adopt the same structure as the derivatives of tetrahedral anions? Both BF_4^- and ClO_4^- anions have three of the four peripheral atoms involved in weak interactions. As

Table 5 Main bond lengths and interatomic distances (Å) and their e.s.d.s in the three compounds[a]

	NO_3^-	BF_4^-	ClO_4^-
Dinuclear entities (atoms labelled d)			
(*a*) Around Cu			
Cu–O(1)	1.983(2)	1.981(2)	1.979(2)
Cu–O(2)	1.975(2)	1.971(2)	1.982(2)
Cu–N(2)	1.981(2)	1.976(2)	1.992(2)
Cu–N(2′)	1.987(2)	1.987(2)	1.987(2)
Cu–O(w)	2.246(2)	2.279(2)	2.285(2)
Cu–X(4)[b]	2.973(7) [X = O(n)]	2.716(2) (X = F)	2.799(2) [X = O(p)]
Cu $\cdots$ Cu^{I}	5.154(1)	5.144(1)	5.150(1)
(*b*) Oxalate bridge			
O(1)–C	1.237(3)	1.253(3)	1.254(3)
O(2)–C	1.254(4)	1.248(3)	1.261(3)
C–C^{I}	1.553(4)	1.533(5)	1.544(6)
Mononuclear entities (atoms labelled m)			
(*a*) Around Cu			
Cu–O(1)	1.912(2)	1.917(2)	1.921(2)
Cu–N(2)	1.956(2)	1.968(2)	1.984(2)
Cu–X(3)[b]	2.833(4) [X = O(n)]	2.579(2) (X = F)	2.605(2) [X = O(p)]
Oxalate			
O(1)–C	1.280(3)	1.262(3)	1.278(3)
O(2)–C	1.217(3)	1.227(3)	1.213(3)
C–C^{II}	1.554(5)	1.557(6)	1.581(6)
Counter ion			
A–X(1)	1.244(2)	1.372(2)	1.423(2)
A–X(2)	1.211(2)	1.339(2)	1.400(2)
A–X(3)	1.295(3)	1.388(2)	1.442(2)
A–X(4)	1.352(6)[b]	1.360(2)	1.394(2)
Hydrogen bonds			
O(wd) $\cdots$ O(2m)	2.788(3)	2.767(3)	2.750(3)
O(wd) $\cdots$ X(1^{III})	2.822(3)	2.945(3)	3.004(3)

[a] Symmetry equivalent positions with respect to *x*, *y*, *z*: I, $\frac{1}{2} - x, \frac{1}{2} - y, -z$; II, $-x, y, \frac{1}{2} - z$; III, $x, 1 - y, z - \frac{1}{2}$. [b] See text.

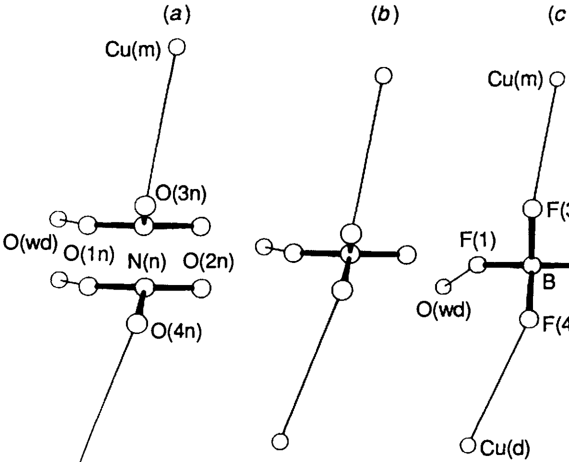

Fig. 4 How the NO_3^- anion mimics a tetrahedral anion: the two configurations of NO_3^- in the nitrato derivative (*a*) are superimposed (*b*) and compared to that of BF_4^- (or ClO_4^-) in the tetrafluoroborate (or perchlorate) derivative (*c*)

Table 6 Bond angles (°) and e.s.d.s in the three compounds

	NO_3^-	BF_4^-	ClO_4^-
Dinuclear entities			
(*a*) Around Cu			
O(w)–Cu–O(1)	94.26(7)	96.48(9)	96.70(8)
O(w)–Cu–O(2)	92.52(7)	90.38(8)	90.65(8)
O(w)–Cu–N(2)	93.56(7)	94.41(9)	94.80(8)
O(w)–Cu–N(2′)	97.70(7)	97.95(9)	98.73(9)
O(1)–Cu–O(2)	84.56(6)	84.87(8)	85.38(6)
O(1)–Cu–N(2)	96.66(7)	95.16(9)	94.72(9)
O(1)–Cu–N(2′)	168.01(7)	165.46(9)	164.53(9)
O(2)–Cu–N(2)	173.69(7)	175.17(9)	175.50(9)
O(2)–Cu–N(2′)	95.61(7)	96.69(9)	95.52(9)
N(2)–Cu–N(2′)	81.90(7)	82.07(9)	82.92(9)
(*b*) Oxalate bridge			
Cu–O(1)–C	111.1(1)	110.5(1)	110.5(2)
Cu–O(2)–C^{I}	111.2(1)	110.5(1)	110.0(2)
O(1)–C–O(2)	127.1(2)	126.1(2)	126.1(3)
O(1)–C–C^{I}	116.9(2)	116.5(3)	116.7(3)
O(2)–C–C^{I}	116.1(2)	117.4(3)	117.1(3)
Mononuclear entities			
(*a*) Around Cu			
O(1)–Cu–O(1^{II})	86.3(1)	85.5(1)	85.5(1)
O(1)–Cu–N(2)	95.21(7)	96.96(9)	96.24(9)
N(2)–Cu–N(2^{II})	86.6(1)	82.9(1)	82.3(1)
(*b*) Oxalate			
Cu–O(1)–C	112.3(2)	112.8(2)	113.6(2)
O(1)–C–O(2)	124.3(2)	125.3(3)	125.9(3)
O(1)–C–C^{II}	114.5(1)	114.5(2)	113.7(2)
O(2)–C–C^{II}	121.2(1)	120.2(2)	120.3(2)
Counter ion			
X(1)–A–X(2)	122.7(1)	110.8(2)	110.3(2)
X(1)–A–X(3)	119.4(2)	109.6(2)	109.4(2)
X(1)–A–X(4)	111.0(2)	110.0(2)	110.9(2)
X(2)–A–X(3)	115.4(2)	108.9(2)	108.6(2)
X(2)–A–X(4)	118.5(2)	112.0(2)	110.6(2)
X(3)–A–X(4)		105.3(2)	107.0(2)
Hydrogen bonds			
O(wd)–H(1wd)–O(2m)	169(2)	139.3(2)	H atoms
O(wd)–H(2wd)–X(1^{III})	157(3)	149.2(2)	not found

For symmetry equivalent position see Table 5.

NO_3^- has only three such atoms, the answer would be straightforward if they were all three involved in these weak interactions: no need for a fourth atom to fix the crystal structure. However, one of the nitrate O atoms, O(2n), is free from any intermolecular contact as are F(2) and O(2p) in BF_4^- and ClO_4^- respectively. Another, O(1n), is hydrogen-bonded to water molecules as are F(1) and O(1p). Therefore, only one nitrate O atom remains to play the bridging role that both X(3) and X(4) of the tetrahedral anions play between Cu(m) and Cu(d). This atom was found distributed over two positions, O(3n) and O(4n), with unequal occupancies: 60 and 40% respectively. The other nitrate atoms show no marked anisotropy as they would do if significantly disordered. The O(3n)–O(4n) segment is nearly perpendicular to the O(1n)–O(2n) segment, and the chemically meaningless O(3n)–N(n)–O(4n) angle is equal to 45.6(3)°. The nitrogen atom is 0.114(2) and 0.256(2) Å from the planes of atoms O(1n),O(2n),O(3n) and O(1n),O(2n),O(4n) respectively. As a result, neither of the two nitrate configurations is planar, and their superposition, which of course has no chemical meaning, is a distorted tetrahedron. The nitrate anion is weakly bound either to a Cu(m) atom by the O(3n) atom at 2.833(4) Å [Fig. 4(*a*)] or to a Cu(d) atom by the O(4n) at 2.973(7) Å [Fig. 4(*b*)]. These distances are consistent with the respective occupancies of 60 and 40%. The alternate chaining of Cu(m) and Cu(d) through BF_4^- and ClO_4^- is no longer possible through NO_3^- (Fig. 4). The fact

Table 7 Atom-to-plane distances (10^{-3} Å) and dihedral angles (°) in the three structures

	NO_3^-	BF_4^-	ClO_4^-
Dinuclear entity			
Plane 1			
O(1d)	−51(2)	−82(2)	−85(2)
O(2d)	51(2)	81(2)	84(2)
N(2d)	52(2)	84(2)	87(2)
N(2′d)	−52(2)	−83(2)	−86(2)
Cu(d)*	155(1)	165(1)	180(1)
Plane 2			
O(1d)	−0(2)	−0(2)	3(2)
O(1d^{I})	0(2)	0(2)	−3(2)
O(2d)	−0(2)	−0(2)	−3(2)
O(2d^{I})	0(2)	0(2)	3(2)
C(d)	2(2)	1(2)	−12(2)
C(d^{I})	−2(2)	−1(2)	12(2)
Dihedral angles			
Plane 1–Plane 2	3.2	10.4	12.1
Mononuclear entity			
Plane 5			
O(1m)	−75(2)	−74(2)	−72(2)
O(1m^{II})	75(2)	74(2)	72(2)
N(2m)	75(2)	74(2)	72(2)
N(2m^{II})	−75(2)	−74(2)	−72(2)
Plane 6			
O(1m)	18(2)	18(2)	15(2)
O(1m^{II})	−18(2)	−18(2)	−15(2)
O(2m)	−17(2)	−16(2)	−22(2)
O(2m^{II})	17(2)	16(2)	22(2)
C(m)	−2(2)	−2(3)	−15(2)
C(m^{II})	2(2)	2(3)	15(2)
Plane 3			
C(1d)	−1(2)	−2(3)	0(2)
N(2d)	4(2)	5(2)	7(3)
C(3d)	−4(2)	−4(3)	−10(3)
C(4d)	−0(2)	−1(3)	5(2)
C(5d)	4(3)	4(3)	2(2)
C(6d)	−3(2)	−3(3)	−5(3)
Plane 4			
C(1′d)	12(2)	9(3)	0(3)
N(2′d)	−4(2)	−2(2)	14(3)
C(3′d)	−7(2)	−6(3)	−15(2)
C(4′d)	10(2)	7(3)	16(2)
C(5′d)	−2(2)	0(4)	−2(2)
C(6′d)	−8(2)	−8(3)	−12(3)
Plane 3–Plane 4	7.1	9.3	10.7
Plane 7			
C(1m)	2(2)	6(3)	2(2)
N(2m)	−1(2)	1(2)	−10(2)
C(3m)	−4(3)	−8(3)	7(3)
C(4m)	7(2)	7(3)	6(3)
C(5m)	−5(3)	−1(3)	−15(3)
C(6m)	−0(2)	−6(3)	11(3)
Dihedral angle Plane 7–Plane 7^{II}	3.0	5.0	5.0
Oxalate torsion around C–C	1.8	1.8	1.7

For symmetry equivalent positions see Table 5.

* Not included in mean-plane calculation.

that the three compounds are isostructural suggests that the crystal structure does not depend on the counter ion but that the packing of the mono- and di-nuclear entities forces a non-tetrahedral anion to mimic a tetrahedron by adopting two configurations the superposition of which resembles a tetrahedron.

Another intriguing feature is the elongation by up to 0.05 Å of bond lengths of the 2,2′-bipyridine ligand in the perchlorate derivative with respect to the other compounds.

Infrared and EPR Spectra.—The IR spectra of oxalate-containing complexes have been thoroughly investigated,[24] and it has been found that the carbon–oxygen stretching frequencies can be diagnostic of the co-ordination modes of the oxalate ligand. Bidentate and bis(bidentate) oxalate coexist in complexes **1**–**3** as evidenced by the above crystallographic study and it seemed very interesting to comment on the IR bands in the 1750–1250 cm^{-1} region attributable to oxalate for such complexes. The spectra of **1**–**3** are nearly identical, the only differences being the bands assigned to the counter ion (NO_3^-, BF_4^- and ClO_4^- for **1**, **2** and **3** respectively). The occurrence of bidentate and bis(bidentate) oxalate is clearly observed: the ν_{asym}(CO) (1720, 1670, 1650 cm^{-1}), ν_{sym}(CO) (1410, 1280 cm^{-1}) and δ(OCO) (780 cm^{-1}) features are characteristic of bidentate oxalate,[24,25] whereas the ν_{asym}(CO) (1645 cm^{-1}), ν_{sym}(CO) (1350, 1315 cm^{-1}) and δ(OCO) (800 cm^{-1}) bands agree well with those reported for bis(bidentate) oxalate in dinuclear copper(II) complexes.[26]

The polycrystalline powder EPR spectra of complexes **1**–**3** at 290 and 4.2 K look like axial doublets with no hyperfine structure. The $g_{\parallel}$ values [2.21(1), 2.20(1) and 2.21(1) for **1**–**3**] being higher than $g_{\perp}$ [2.06(1), 2.05(1) and 2.06(1) for **1**–**3**] are indicative of a $d_{x^2-y^2}$ ground state. The g values are in agreement with those for CuO_2N_2 chromophores with strong planar bonding and weaker axial bonding. A weak absorption at half field arising from a $\Delta M_s = 2$ forbidden transition in the populated triplet is observed at 290 K for all three complexes. Therefore, IR and EPR spectra strongly support the existence of mono- and di-nuclear entities in the series **1**–**3**.

Magnetic Properties.—The thermal variation of the molar susceptibility of complex **1** is shown in Fig. 5 as the product $\chi_M T$ *versus* T. Similar curves are obtained for complexes **2** and **3**. The product $\chi_M T$ decreases upon cooling and exhibits a plateau when $T < 80$ K in all three cases. The smooth decrease in the range 300–80 K is indicative that an antiferromagnetic interaction larger than 300 cm^{-1} is operative within the dinuclear unit, while the plateau corresponds to the Curie law expected for the mononuclear complex with no detectable interaction between the two kinds of entities in the 300–20 K temperature range. The experimental data closely follow the relation (1)

$$\chi_M = (2N\beta^2 g_d^2/kT)[3 + \exp(-J/kT)]^{-1} + (N\beta^2 g_m^2/4kT) + N\alpha \quad (1)$$

which is the sum of the Bleaney–Bowers equation for a coupled dinuclear copper(II) species, the Curie law for an isolated copper(II) complex, and the temperature-independent paramagnetism, $N\alpha$; J is the singlet–triplet energy gap and g_d and g_m

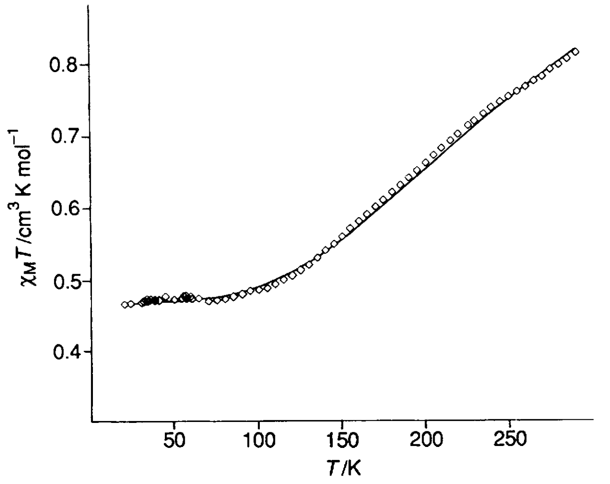

Fig. 5 Thermal variation of the susceptibility of complex **1** in the range 20–300 K [☐, experimental data; –, theoretical curve]

Table 8 Best-fit magnetic data and agreement factors

Complex	J/cm^{-1}	g_d	g_m	$10^5 R$*
1	−386	2.003	2.217	5.40
2	−378	2.00	2.20	6.53
3	−376	2.01	2.23	6.99

* The agreement factor defined as $[\Sigma(\chi_M T)^{obs} - (\chi_M T)^{calc}]^2/\Sigma[(\chi_M T)^{obs}]^2$.

are the mean g factors for the di- and mono-nuclear complexes. Least-squares fit of the experimental data for **1**–**3** by a Simplex method leads to the J, g_d and g_m values listed in Table 8.

A practically identical and strong antiferromagnetic coupling is observed in all three complexes. Considering the structure of this series of complexes, two different exchange pathways are possible: one through the oxalato bridge within the dinuclear unit and the other through the counter ion that links alternatively mono- and di-nuclear entities. The unpaired electron of each copper(II) ion within the dinuclear units is described by a magnetic orbital which points towards the nearest neighbours O(1d), O(2d), N(2d) and N(2′d) in the plane of the oxalato bridge. Similarly, a magnetic orbital pointing toward atoms N(2m), N(2m^{II}), O(1m) and O(1m^{II}) describes the unpaired electron of copper(II) in the mononuclear complex. Since the axial distances around copper(II) are longer than the equatorial ones, the admixture of the d_{z^2} orbital in the $d_{x^2-y^2}$ ground state is weak, and consequently the overlap between parallel $d_{x^2-y^2}$ orbitals of mono- and di-nuclear units separated by more than 5.5 Å in **1**–**3** is expected to be very small. It is well known that in these systems the magnitude of J is essentially governed by S^2, the square of the overlap integral between the magnetic orbitals.[1b,2,3,27] This rules out a strong interaction through the counter ions in **1**–**3**. On the other hand, an oxalate bridge is known to be very effective in transmitting exchange interaction when the σ in-plane overlap between $d_{x^2-y^2}$ orbitals is operative.[1,28]. The large couplings in this series arise from the important overlap of the $d_{x^2-y^2}$ magnetic orbitals through the symmetry-adapted highest-occupied molecular orbitals of the oxalate ligand. The high J values of this series is a new confirmation of the remarkable efficiency of the oxalate bridge to transmit electronic effects between copper(II) ions separated by more than 5 Å.

Despite the alternating chain arrangement of mono- and di-nuclear units in this series of complexes, the observed magnetic behaviour can easily be interpreted by means of a simple Bleaney–Bowers expression [equation (1)]. Magnetic susceptibility measurements at $T < 20$ K evidence the existence of a very weak interaction between the mono- and di-nuclear units but we have not further explored this low-temperature magnetic behaviour.

Finally, the concept of a magnetic orbital which is defined in hypothetical mononuclear species materializes in this series in the mononuclear entity and the structures reported illustrate for the first time the coexistence of the $d_{x^2-y^2}$ magnetic orbital of the mononuclear fragment and its combination through the oxalato bridge in the dinuclear species.

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